

**DEVELOPMENT OF A LINEAR ION TRAP MASS SPECTROMETER (LITMS) INVESTIGATION FOR FUTURE PLANETARY SURFACE MISSIONS.** W. Brinckerhoff<sup>1</sup>, R. Danell<sup>2</sup>, F. van Amerom<sup>3</sup>, V. Pinnick<sup>4</sup>, X. Li<sup>4</sup>, R. Arevalo<sup>1</sup>, D. Glavin<sup>1</sup>, S. Getty<sup>1</sup>, P. Mahaffy<sup>1</sup>, P. Chu<sup>5</sup>, K. Zacny<sup>5</sup>, S. Rogacki<sup>6</sup>, A. Grubisic<sup>7</sup>, T. Cornish<sup>8</sup>

<sup>1</sup>NASA Goddard Space Flight Center (8800 Greenbelt Road, Mailstop 699, Greenbelt, MD 20771) william.b.brinckerhoff@nasa.gov; <sup>2</sup>Danell Consulting, Inc., Winterville, NC; <sup>3</sup>Mini-Mass Consulting, Hyattsville, MD; <sup>4</sup>Center for Research and Exploration in Space Science and Technology (CRESST), University of Maryland, Baltimore County, Baltimore, MD; <sup>5</sup>Honeybee Robotics Spacecraft Mechanisms Corp., New York, NY; <sup>6</sup>Space Physics Research Laboratory (SPRL), University of Michigan, Ann Arbor, MI; <sup>7</sup>CRESST, University of Maryland at College Park, College Park, MD; <sup>8</sup>C & E Research, Inc., Columbia, MD.

**Introduction:** Future surface missions to Mars and other planetary bodies will benefit from continued advances in miniature sensor and sample handling technologies that enable high-performance chemical analyses of natural samples. Fine-scale (~1 mm and below) analyses of rock surfaces and interiors, such as exposed on a drill core, will permit (1) the detection of habitability markers including complex organics in association with their original depositional environment, and (2) the characterization of successive layers and gradients that can reveal the time-evolution of those environments. In particular, if broad-based and highly-sensitive mass spectrometry techniques could be brought to such scales, the resulting planetary science capability would be truly powerful.

The Linear Ion Trap Mass Spectrometer (LITMS) investigation is designed to conduct fine-scale organic and inorganic analyses of short (~5-10 cm) rock cores such as could be acquired by a planetary lander or rover arm-based drill. LITMS combines both pyrolysis/gas chromatograph mass spectrometry (GCMS) of subsampled core fines, and laser desorption mass spectrometry (LDMS) of the intact core surface, using a common mass analyzer, enhanced from the design used in the Mars Organic Molecule Analyzer (MOMA) instrument on the 2018 ExoMars rover [1]. LITMS additionally features developments based on the Sample Analysis at Mars (SAM) investigation on MSL and recent NASA-funded prototype efforts in laser mass spectrometry, pyrolysis, and precision subsampling.

LITMS brings these combined capabilities to achieve its four measurement objectives:

(1) Organics: Broad Survey Detect organic molecules over a wide range of molecular weight, volatility, electronegativity, concentration, and host mineralogy.

(2) Organic: Molecular Structure Characterize internal molecular structure to identify individual compounds, and reveal functionalization and processing.

(3) Inorganic Host Environment Assess the local chemical/mineralogical makeup of organic host phases to help determine deposition and preservation factors.

(4) Chemical Stratigraphy Analyze the fine spatial distribution and variation of key species with depth.

**Approach:** The concept of dual ion source mass spectrometry applied to fine-scale analysis of a core on a Mars mission is shown conceptually in **Figure 1**. The acquired core is captured in a bit featuring an oblong open window, such as the PreView Bit design developed by Honeybee Robotics (1). Once engaged in the LITMS core sampling station, the drill's linear (2) and rotational (3) motion combined with a passive counter-spring enables fine positioning of the core under the inlet for non-destructive Mars-ambient LDMS analysis with adjustable laser spot diameter in the range 100-200  $\mu\text{m}$ . Data from selected points or layers on the core surface are then used to prioritize one or more core positions from which to obtain a powder subsample for pyrolysis GCMS. The chosen position (e.g., layer) is then positioned where a high-speed grinding wheel (4) engages the core (5) delivering up to several mg of fines to a pyrolysis oven (not shown) via a funnel (6). This approach assures complementary analyses of the same point (red dot in Fig. 1), alleviating the typical but critical issue of comparability when studying natural samples with separate instruments.

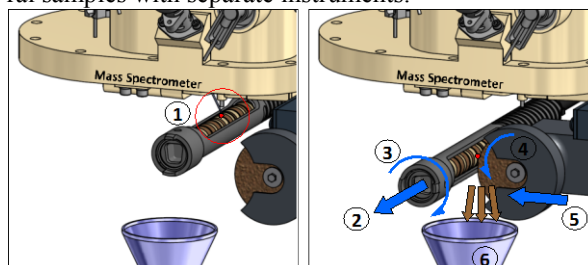


Fig. 1 The LITMS measurement approach involves positioning of a core sample in a PreView Bit, or other holding fixture, and configurations for LDMS (left) and pyrolysis GCMS (right). Following LDMS analysis of nonvolatile composition at selected points or layers on the core, one or more layers (nominally normal to the core axis, as shown) are subsampled for pyrolysis followed by direct evolved gas analysis (EGA-MS) and GCMS of more volatile compounds.

**Analytical Features:** LITMS comprises the MS subsystem (including ion trap, pump, valves, and RF and DC voltage supplies), the precision sampler, high-

temperature pyrolysis and GC subsystems, and a pulsed UV laser, with associated control electronics. Selected capability enhancements for LITMS, compared to existing instruments, are under development with support of the Maturation of Instruments for Solar System Exploration (MatISSE) program; the main enhancements are listed in Table 1, compared to the relevant existing capabilities. These are undergoing testing individually on breadboards of the MOMA mass spectrometer, ovens following designs from SAM and from the Volatile Analysis by Pyrolysis of Regolith (VAPoR) instrument [2], coring and subsampling hardware from prior Mars Instrument Development Project (MIDP) efforts, and selected LITMS-specific prototypes. The MatISSE goal is to develop a LITMS brassboard based on these tests and to conduct end-to-end testing in a Mars-relevant environment.

Table 1 LITMS features enhancements in key measurement-enabling capabilities geared to the broadest-possible investigation of organic and their host inorganic species on a fine scale in drill cores (nominally 1 cm diameter x 5-10 cm long). More precise laser energy control and temperature tracking, compared to MOMA, improves analytical flexibility and validation of calibrated scientific results.

Specification Requirement	Existing (MOMA or SAM)	LITMS
core handling	none	ϕ 1 cm x L 5-10 cm
m/z range	50 – 1000 Da	20 – 2000 Da
m/z peak width	≤ 1 Da (50-500 Da) ≤ 2 Da (to 1000 Da)	≤ 0.5 Da (20-300 Da) (as MOMA > 300 Da)
ion detection	positive only	positive & negative
spatial resolution	none (powder)	LDMS: ≥ 0.1 mm GCMS: ≥ 1 mm
laser energy	10%-100% linear via passive q-sw. temp.	1%-100% logarithmic via pockels cell
pyrolysis temp.	1100 C max.	1300 C max.

**LDMS Mode.** The surface of the core is close enough (~3 mm) to the inlet to allow Mars-ambient laser desorption/ionization of the surface using pulsed UV laser, with positive or negative ions, that would otherwise thermalize in the ~5-7 torr martian atmosphere, drawn across the gap in a modest electric field. As they approach the inlet, ions are entrained in the flow of Mars atmosphere through the tube generated by a small turbo-molecular drag pump (based on the SAM wide range pump). As in the MOMA design, which by contrast conducts Mars ambient LDMS on drill fines loaded onto a refillable tray, the laser produces parent and fragment ions of nonvolatile organic and inorganic species over a wide range of molecular weights. After the ions have passed into the trapping field of the mass

analyzer, a custom gate valve immediately closes off the tube, causing the trap pressure to reduce within ~1 second to the sub-mtorr range, where it is safe to operate the high voltage detectors. This two-step valved scheme follows the discontinuous atmospheric pressure ionization (DAPI) approach [3] removing any requirement for vacuum sealing of samples. An additional benefit of using the short pulsed (1 ns) laser is that complex organics are volatilized and ionized intact, even in the presence of oxidizing compounds such as perchlorate salts [4].

**Precision Core Sampling.** Core subsampling using a rotating grinder (at speeds of 1-5 krpm) produces between 0.1 – 5 mg of fines in 30 seconds, depending on the rock type. While sufficient for complete pyrolysis analysis, this sample mass is not significant compared to the ~10 g core, implying that many such subsamples can be extracted from each core. Significant efforts have been applied to characterize the behavior of subsampled fines, to maximize grinder efficiency and operational life, and to minimize cross contamination by fine particulate. In Mars ambient conditions, fines are observed to follow predictable trajectories, with short settling times owing to the low pressure compared to Earth. Piezoelectric excitation such as used on SAM is applied to the short funnel to quantitatively deliver fines into one of several (nominally 24) pyrolysis ovens arrayed on a compact carousel.

**GCMS Mode.** The VAPoR-derived LITMS pyrolysis system is able to heat samples from ambient to a maximum temperature of 1300° C using a programmed step or linear ramp, providing more complete coverage and separation of both mineral and hydrocarbon volatile decomposition products (H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub>, HCl, O<sub>2</sub>, alkane and aromatic hydrocarbons) from a wide mineral phases including phyllosilicates, sulfates, and carbonates [2]. This maximum temperature significantly exceeds previous spaceflight pyrolysis systems while reducing the peak power required to approximately 30 W compared with more than 40 W for SAM (at 1000 °C) by maintaining heating elements with each alumina cup. The small internal volume and sample mass, along with carefully-arranged multilayer rhodium and tungsten shields, also help minimize power. Temperature tracking is more precise with the incorporation of thermocouples in the cup base. The LITMS design supports direct EGA with a dedicated gas “bypass” line and dedicated leak into the electron ionization source of the MS. The GC design, provided by the University of Paris, follows the MOMA (and SAM) design, but is limited to two columns to minimize mass and simplify plumbing.

**Preliminary Development and Testing** We have carried out a number of LITMS development and testing tasks to reach Year 1 laboratory milestones. Here we provide some information on two developments: (1) improvements in mass range and resolution with the addition of a high-frequency RF source, and (2) analysis of the benefit of including a negative ion mode.

**Mass Range and Resolution.** To expand the  $m/z$  range (to 20-2000 Da) while maintaining resolution, accuracy, drift, and noise specifications, LITMS includes a two-frequency RF system. The MOMA single RF frequency of 1 MHz covers  $m/z$  50-1000, while higher  $m/z$  ions are still trapped and detected with somewhat lower resolution and sensitivity. Higher frequencies reduce the low-mass cutoff (LMC) in an ion trap (lighter ions have to be “turned around” more frequently to remain trapped). LITMS thus baselines a combination of a lower frequency (600 kHz), for  $m/z$  100-2000, and a higher frequency (1.5 MHz), for  $m/z$  20-300, each appropriately tuned. Various interleaving strategies are under consideration for switching mass ranges during instrument operations.

As an initial test of the impact of higher frequency operation, a breadboard supply capable of frequencies in the range 1.5-2.0 MHz was developed and operated with a LITMS prototype, derived from MOMA. The tuning compound perfluoro-tributylaine (PFTBA) was used (at 5 ppmv) in He for straightforward EI tests.

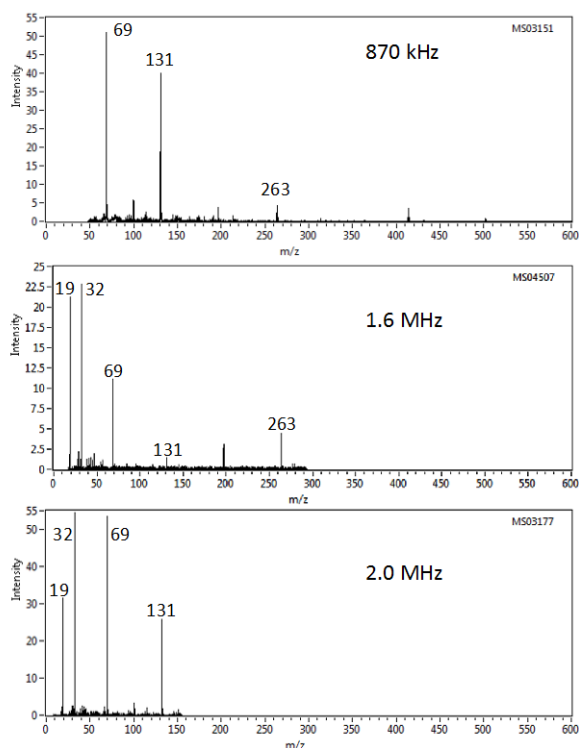


Fig. 2 Comparison of LITMS electron ionization (EI) spectra of PFTBA in He, using different main RF frequencies.

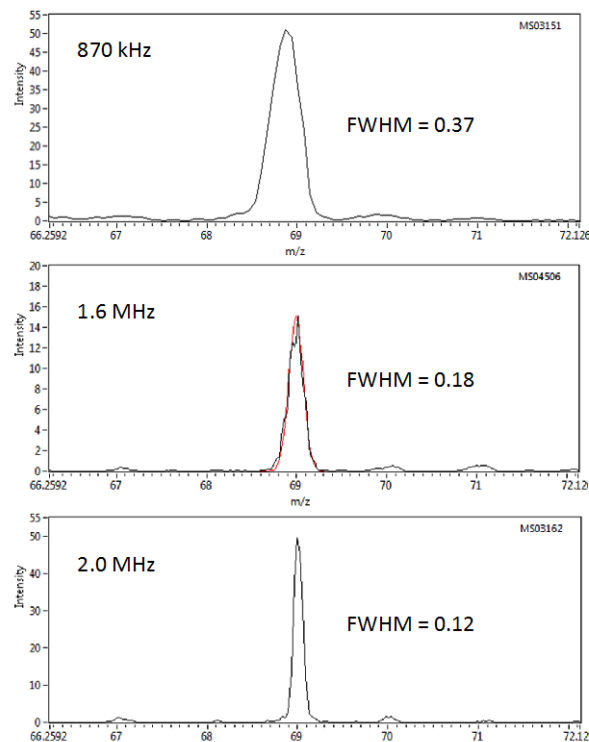
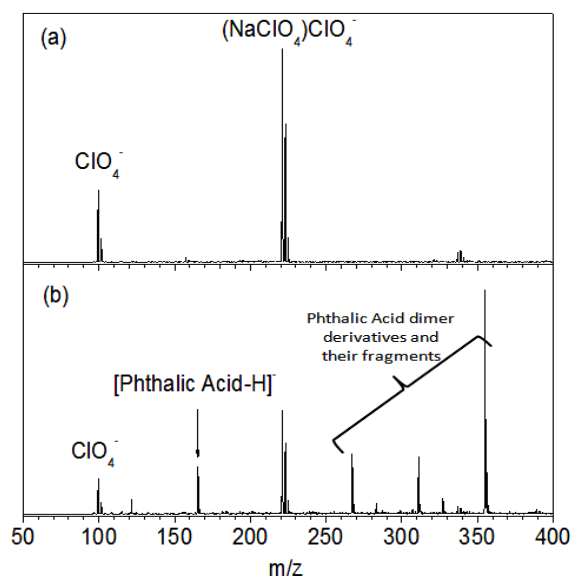


Fig. 3 Comparison of LITMS electron ionization (EI) spectra of PFTBA in He, using different main RF frequencies. Focus on the range near  $m/z$  69 to show narrowing peak widths.

**Figure 2** compares example PFTBA fragment spectra between MOMA-class (870 kHz) and higher (1.6 and 2.0 MHz) frequencies. In this EI mode the MOMA-like supply exhibits the expected distribution of peaks over the nominal  $m/z$  range 50-500 Da. At 1.6 MHz the intense  $m/z$  19 ( $F^+$ ) and  $m/z$  32 ( $O_2^+$ ) peaks are readily detected, with the upper trapped  $m/z$  in the 300 Da range as expected. Pushing the frequency to 2.0 MHz lowers the LMC even further, to  $m/z$  12, while limiting the mass range to  $\sim 150$  Da. In **Figure 3**, the increase of mass resolution with higher frequency operation is also observed by comparing peak widths of the  $m/z$  69 signal. Improving resolution with a fixed number of trapped ions has the additional benefit of higher signal-to-noise ratio (SNR) as the detected ions drive the peak intensity up sampling a greater single-ion dynamic range. The selection of 1.5 MHz for the higher of two frequencies in the planned LITMS brassboard RF supply is thus validated per **Table 1**.

**Negative Ion Analysis.** Complementary information from negative ion LDMS improves identification of electronegative moieties, containing elements such as S and Cl, as well as classes of organics (including several carboxylic and amino acids) that favor anion formation. Negative mode spectra additionally lack the intense peaks from Na, K and their adducts; the strong signals produced by their counterpart cations often

plague positive mode spectra, effectively diluting trace signals from other rock-forming elements or organic molecules particularly in the mass range 25-150 Da. Negative ion detection also improves the capacity to detect organics in the presence of the strong oxidant perchlorate ( $\text{ClO}_4^-$ ), which has been measured at high levels (up to 0.7 wt.%) in the Martian soil by the Phoenix Mars Lander [5,6]. Perchlorates could have presented analytical challenges to the pyrolysis experiments on Viking and Phoenix [7], and may do so on MSL. We routinely conduct negative ion mode LDMS studies of synthetic analogs containing silicate or other minerals, organic spikes, and up to several weight % levels of perchlorate salt. The organic species are readily volatilized and ionized by the extremely short energy burst ( $\sim 1$  ns) provided by laser desorption, without oxidative degradation. **Figure 4** shows negative ion mass spectra, from a Thermo Scientific LTQXL linear ion trap which serves as a close analog for LITMS. NIST SRM81A reagent sand was spiked with 1 wt.% sodium perchlorate, both without (a) and with (b) a phthalic acid spike. The perchlorate anion is a dominant feature in the spectrum at 99 Da and 101 Da. While the LTQ has a low mass cut at 50 Da; LITMS is able to observe the isotopes of Cl at masses 35 Da and 37 Da. Even in the presence of perchlorate salts, the deprotonated molecular ion of phthalic acid was observed at 165 Da. In other tests, we have detected other carboxylic acids and amino acids in mineral mixtures, since these species exhibit a strong preference to form negative ions when desorbed from minerals.



**Fig. 4** Negative mode LDMS spectra of a sand + 1% perchlorate mixture without (a) and with (b) phthalic acid, demonstrating detection of organic signatures in the presence of an oxidizing agent.

**Path Forward:** The main development goal for LITMS in the next year will be to develop the brassboard analogous to the engineering test unit (ETU) of the MOMA mass spectrometer, combined with the precision sampling and pyrolysis subsystems. A two-frequency RF supply will be developed to integrate directly to the MS housing permitting end-to-end testing of both EGA (EI) and LDMS modes. GCMS will then be tested using both commercial and as-available MOMA-type GC columns. The negative ion mode will be implemented in the MS brassboard following testing of a new dynode and channel electron multiplier (CEM) configuration in the existing prototype. Once laboratory brassboard checkouts are complete, using reference core samples, the instrument will be incorporated in a Mars chamber setup at Honeybee Robotics. A rover mockup will support a five degree-of-freedom (5-DOF) robotic arm, the Rotary Percussive Corer (ROPEC) drill, and an updated precision sample grinder. A procedure for determining core quality, integrity, and analysis targets, based on ambient imaging, will also be incorporated into the test campaign to prove out operational concepts for LITMS.

#### References:

- [1] Brinckerhoff W. et al. (2013) *IEEE Aerospace Conference 2013*.
- [2] Glavin D. et al. (2012) *Int. Workshop Instrum. Planet. Missions*, Abstract 1015.
- [3] Gao L. et al. (2008) *Analytical Chemistry* 80: 4026-4032.
- [4] Li X. et al. (2014) *Astrobiology* (submitted).
- [5] Hecht M. et al. (2009) *Science* 325: 64-67.
- [6] Kounaves S. et al. (2009) *J. Geophys. Res.* 115: E00E10 doi: 10.1029/2009JE003424.
- [7] Navarro-González R. et al. (2010) *J. Geophys. Res.*, 115: E12010, doi:10.1029/2010JE003599.